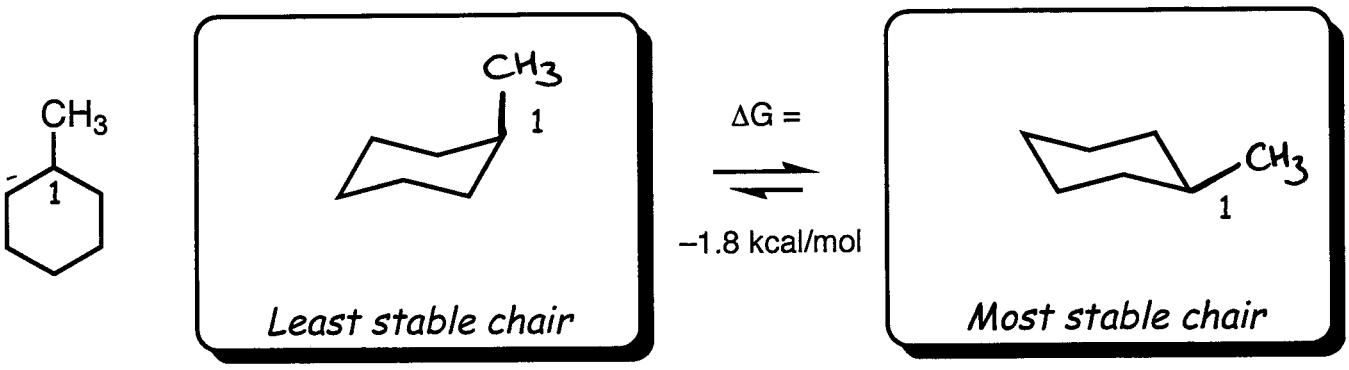
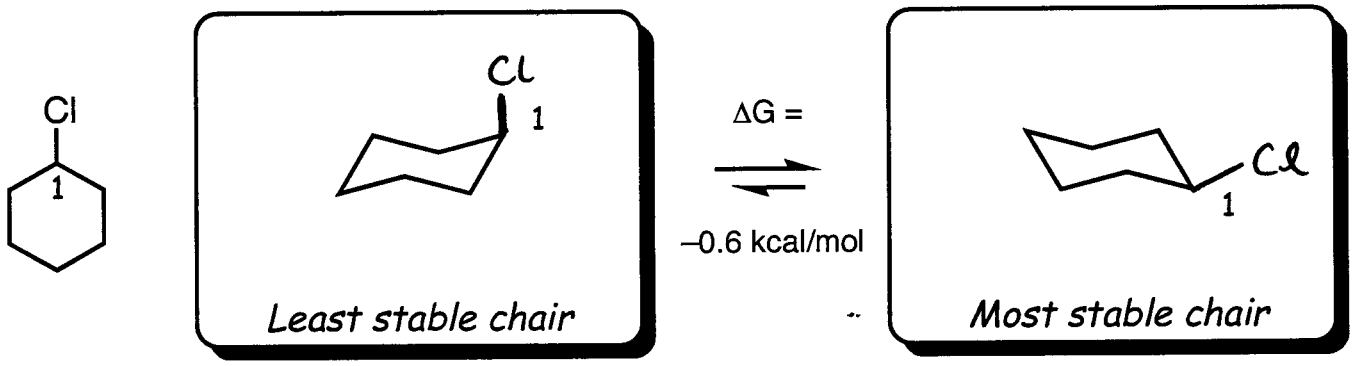
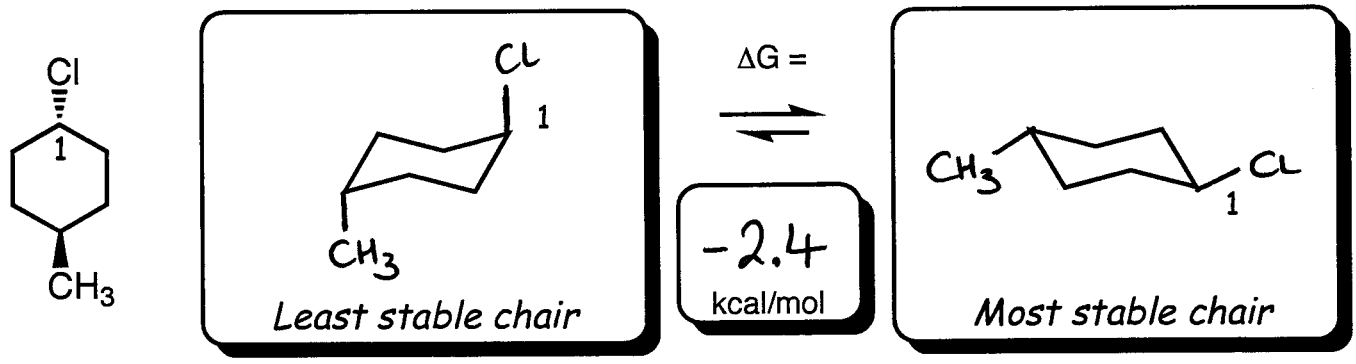
Q3. (a) Methylcyclohexane can exist in two different chair conformations, one of which is 1.8 kcal/mol more stable than the other, i.e., the **A value** for the methyl group is 1.8. In each of the two boxes below, draw in a bond to one methyl ($\mathbf{CH_3}$) group in the appropriate position. (2 pt)



(b) Chlorocyclohexane also exists in two different chair conformations, one of which is 0.6 kcal/mol more stable than the other, i.e., the **A value** for the chloro group is 0.6. In each of the two boxes below, draw in a bond to one chloro (**Cl**) group in the appropriate position. (2 pt)

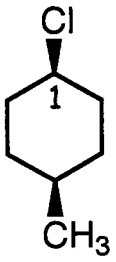


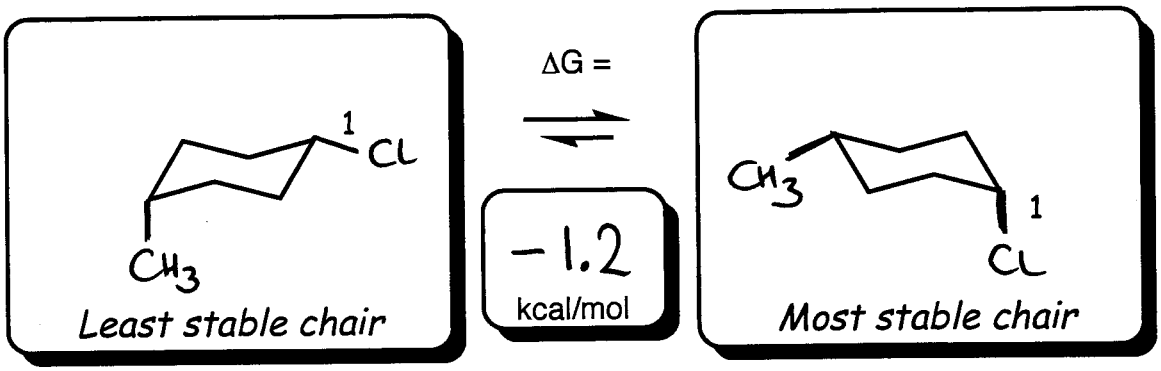
(c) For *trans*-1-chloro-4-methylcyclohexane (shown below), draw in bonds to $\mathbf{CH_3}$ and **Cl** groups as appropriate, to indicate the least and most stable chair conformers. Assuming that **A values** are additive (and hence subtractive if necessary...), predict what the ΔG value will be. (6 pt)



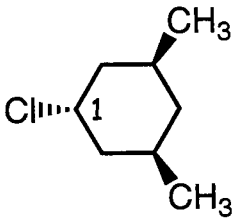
Question 3 is continued on the next page...

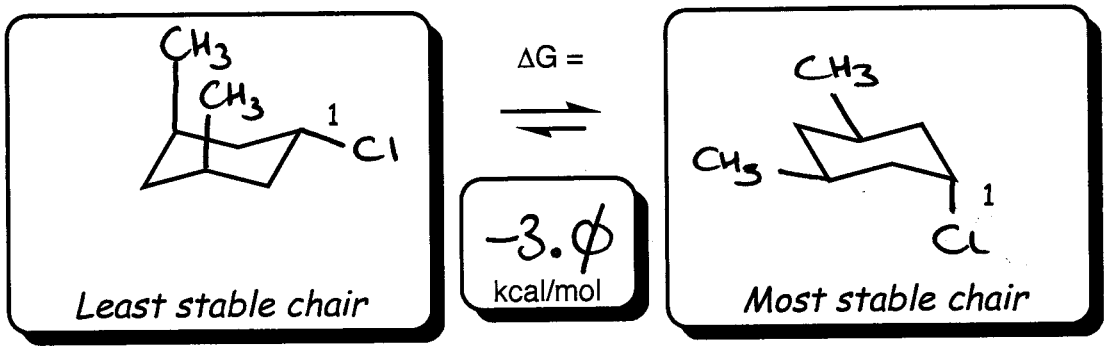
(d) For *cis*-1-chloro-4-methylcyclohexane (shown below), draw in bonds to **CH_3** and **Cl** groups as appropriate, to indicate the least and most stable chair conformers. Assuming that **A values** are additive (and hence subtractive if necessary...), predict what the ΔG value will be. (6 pt)



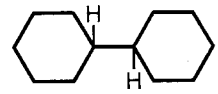


(e) For the isomer of 1-chloro-3,5-dimethylcyclohexane shown below, draw in bonds to **CH_3** and **Cl** groups as appropriate, to indicate the least and most stable chair conformers. Assuming that **A values** are additive (and hence subtractive if necessary...), predict what the ΔG value will be. (8 pt)

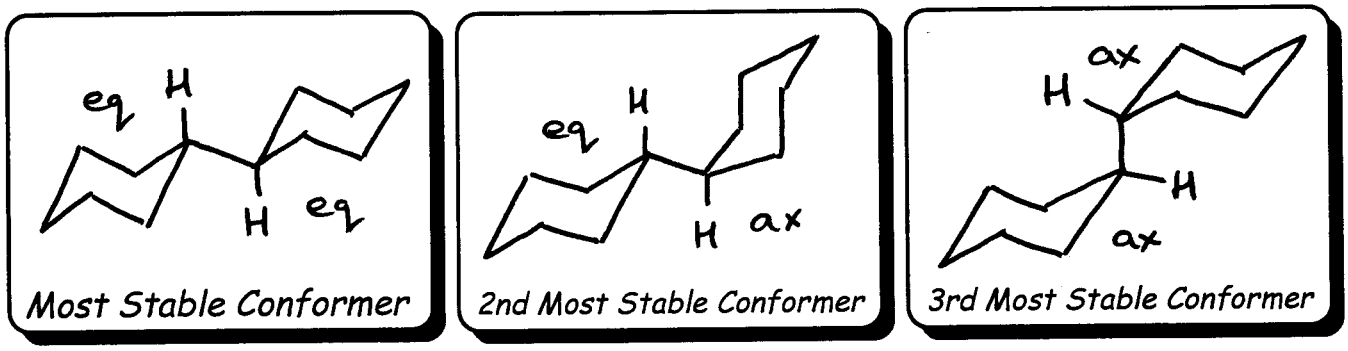




(f) In the appropriate boxes below, draw the three most stable conformations of cyclohexylcyclohexane (shown to the right) in which the indicated H atoms maintain an **ANTI** relationship, i.e., are 180° apart. Once you have drawn these three **different** conformers, use the box below them to briefly explain your answers. (12 pt)

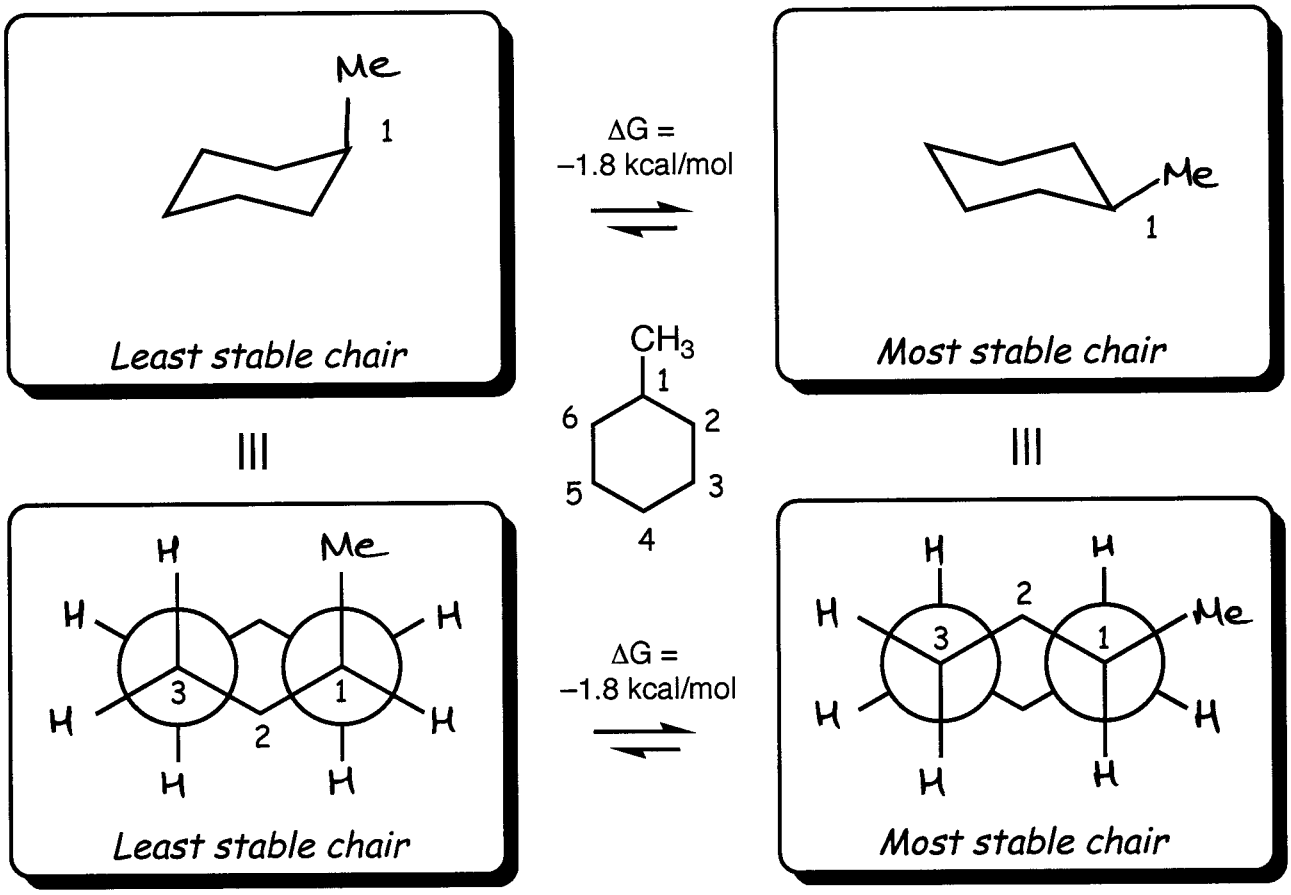


Cyclohexylcyclohexane

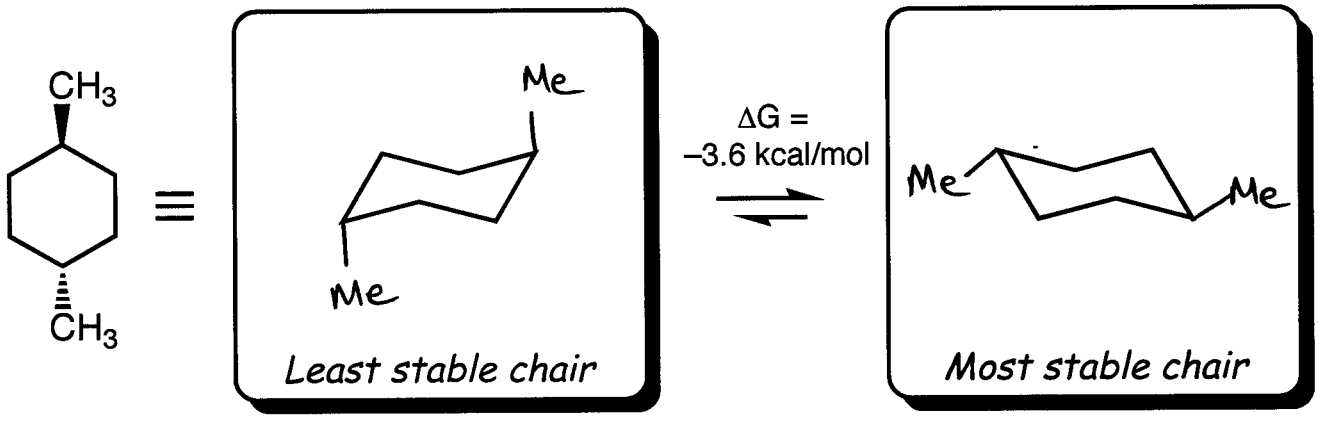


Explanation: ALL RINGS ARE CHAIRS, BUT CAN BE CONNECTED DIFFERENTLY, EQUATORIAL-EQUATORIAL IS MOST STABLE, AXIAL-AXIAL IS LEAST STABLE, AND EQUATORIAL-AXIAL FALLS INBETWEEN

Q3. **(a)** Methylcyclohexane (shown in the middle below) can exist in two different chair conformations, one of which is 1.8 kcal/mol more stable than the other. In each of the top two boxes below, draw in a bond to one methyl (Me) group in the appropriate position. In the bottom two boxes, complete the Newman projections by filling in methyl (Me) groups AND hydrogen atoms (H) where appropriate. (4 points)

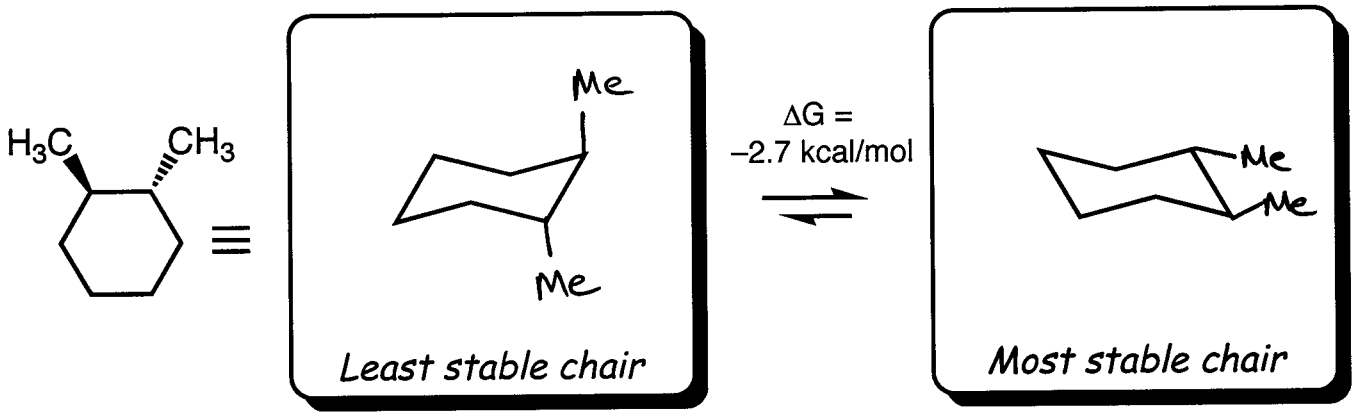


(b) *trans*-1,4-Dimethylcyclohexane (shown below) also exists in two different chair conformations, one of which is **3.6 kcal/mol** more stable than the other. In each of the boxes below, draw in methyl (Me) groups in the appropriate positions. (4 points)



Question 3 is continued on the next page...

(c) *trans*-1,2-Dimethylcyclohexane (shown below) also exists in two different chair conformations, one of which is **2.7 kcal/mol** more stable than the other. In each of the boxes below, draw in methyl (Me) groups in the appropriate positions. (4 points)

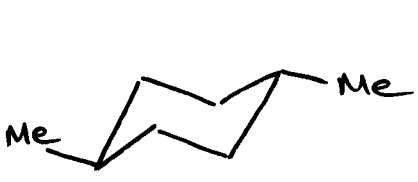


(d) In the box below, explain (using appropriate diagrams if you wish), why the difference in energy between the two chair conformations of *trans*-1,2-dimethylcyclohexane is **0.9 kcal/mol** LESS than the difference in energy between the two chair conformations of *trans*-1,4-dimethylcyclohexane. (8 points)

THE DIAXIAL CONFORMERS OF THE 1,2 AND 1,4 ISOMERS ARE EQUALLY BAD - EACH HAS TWO AXIAL METHYL GROUPS, HENCE THERE ARE 4 BUTANE GAUCHE INTERACTIONS.

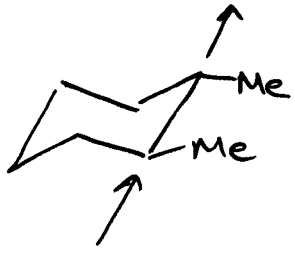
NOW CONSIDER THE DIEQUATORIAL CONFORMERS:

1,4



NO GAUCHE INTERACTIONS,

BUT



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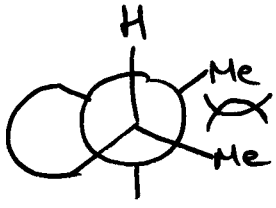
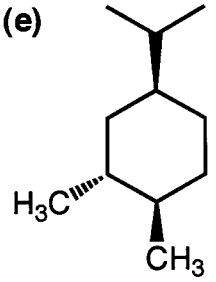


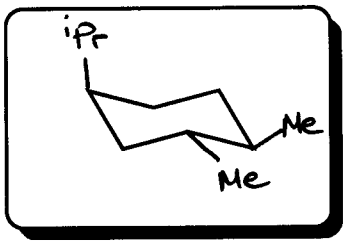
1 GAUCHE INTERACTION, SO DESTABILIZES BY 0.9 kcal/mol.

Question 3 is continued on the next page...

For each of the questions below (**e–h**) draw the most stable chair conformation for each compound, and in each case give a succinct reason for your choice. (*Hint: the answers aren't perhaps as easy as you may think they are...*) (2 + 2 points each)

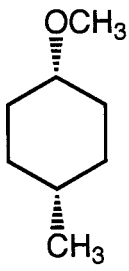
(e)

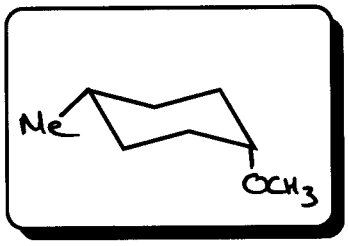




reason:
'A' value for 'Pr, is not much larger than for Me, so better to have two methyls equatorial and one 'Pr axial than vice-versa

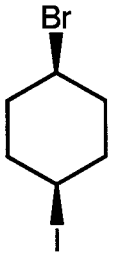
(f)

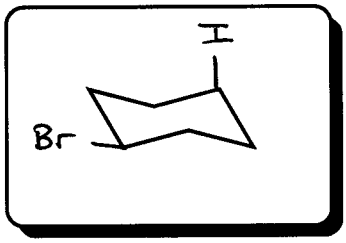




reason:
OCH_3 group can swing away from the ring, and so has less diaxial interactions than an Me group. 'Lone pair vs 'H' into ring

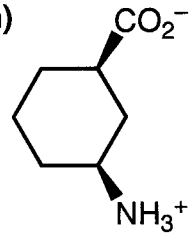
(g)

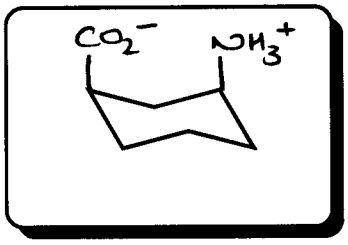




reason:
'I' is bigger than 'Br', but the C—I bond is longer, and so there are less 1,3 diaxial interactions with C—I than C—Br.

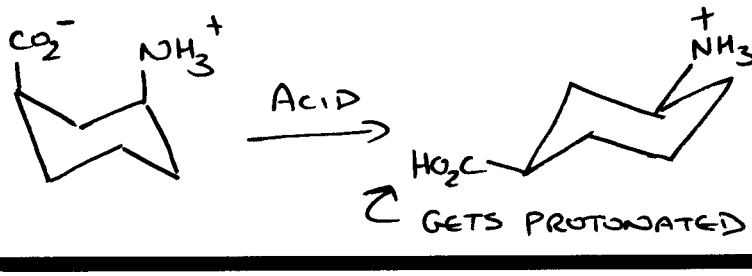
(h)





reason:
The diaxial interactions are bad, but the electrostatic attraction of opposite charges are enough to overcome this.

(i) When the compound in part (**h**) is treated with a strong acid, a new compound is formed. Draw the most stable chair conformation of this new product and justify your choice (4 points)



NO LONGER ANY ELECTROSTATIC ATTRACTION TO OVERCOME BAD STERICS - DIEQUATORIAL IS FAVORED